Activation Analysis As A Tool For The Assignment Of Mode Of Occurrence
  Of Trace Elements In Phosphate Ores

by

L.A. GUIRGUIS AND MARGUERITE A. WASSEF*

17

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie.
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Activation Analysis As A Tool For The Assignment Of Mode Of Occurrence Of Trace Elements In Phosphate Ores

L.A. GUIRGUIS AND MARGURITE A. WASSEF*

Nuclear Material Corporation, Cairo, Egypt
(Received October 19, 1981: accepted December 14, 1981)

ABSTRACT

An efficient calcination process for calcareous phosphate ores is studied as a base for the present work. The net result of the behaviour of the constituent minerals is given.

As determined by a nondestructive neutron activation analysis technique, the trace elements, Ce, Lu, U, Cr, La Hf, Zr Sc and Co are found to be associated with the phosphate mineral while Eu is present in the gangue minerals, as calcite, dolomite, clay and iron oxides. The two elements Ba and Fe are incorporated in both the gangue and the phosphate minerals.

INTRODUCTION

Apatite (the major mineral constituent of phosphate rock) is host to many substitutions by cations, anions, and anionic radicals that resemble its normal constituents in size and charge (1). Accordingly, apatite prove to be a useful environmental indicator.

The major and minor element composition of phosphoritities is naturally of more than academic interest in view of the use of these rocks in the manufacture of fertilizers and phosphoric acid and also because of the feasibility of the byproduct extraction of vanadium, uranium (2), fluorine (3) and the rare earth elements (4). Thus many authors (5-9) have studied the distribution of trace elements in different deposits spectro chemically.

In the present study the distribution and abundance of trace elements in the phosphate mineral or gangue minerals prove to be use-

*Chemistry Dept., University College for Women, Ain Shams University, Cairo, Egypt.
ful, since some of these trace elements such as iron if found in the phosphate minerals are incorporated in the phosphate fertilizer and hence are of great value to certain soils (10). To the knowledge of the present authors no similar study as the present one has been done before, except for uranium and phosphorus which are determined chemically during the physical upgrading of phosphatic sandstone of Egyptian Qatrani ore by flotation (11).

Phosphate ores are usually associated with calcareous materials mainly calcite, dolomite and rarely siderite which lower the phosphate grade. The method used for upgrading these ores is accomplished by calcination to decompose the carbonate into oxides then quenching and washing removing the oxide as a milky solution to obtain the maximum phosphate oxide ratio. In the present work, calcination of the phosphate rock is chosen as the proper technique to separate the phosphate mineral from the gangue minerals.

The development of high resolution Ge (Li) detectors for gamma spectrometry, and efficient data processing systems for spectral analysis, have made instrumental neutron activation analytical methods a powerful analytical tool for multielement determinations (12).

Fortunately, the elements, P,C,O,F and Ca which are considered an interfering elements are either a beta emitter or gamma emitter of a very short half-life; hence their activities decay to negligible proportions before commencing measurements, since a decay time of two days was used. Accordingly, matrix interference was negligible. There was no interference of phosphorous by its bremsstrahlung due to the high resolution of the detector used and the peak to compton area is very high.

Experimental

The phosphate ore presently investigated is a representative sample from Wassif Mine (Red Sea Coast). Calcination of the studied sample was performed using a locally made tube furnace of 60 cm long, 2.5 cm internal diameter. It was connected with a liquid flowmeter to adjust the flow of oxygen gas through the furnace.

A flow rate of $\frac{1}{3}$ L/min was found suitable. The temperature was kept constant at 940 °C for half an hour during the experiment by
means of an automatic regulator. 25 g. sample was placed in a fused magnesite boat and inserted inside the tube furnace.

The calcined sample was removed from the furnace while het in 25 ml of distilled water, washed 4 times while stirring for 5 min. with 50 ml solution of (50 g NH₄ Cl / l). The latter has greatly facilitated the elimination of the lime and magnesia produced during calcination. For the purpose of recycleM the produced NH₄OH could be distilled of and allowed to react with rock salt regenerating NH₄Cl and NaOH. The overall reactions involved could be summarized in the following equations.

\[
\begin{align*}
CaMg(CO₃)₂ & \rightarrow CaCO₃ + Mg + CO₂ \\
Ca CO₃ & \xrightarrow{ΔH} CaO + CO₂ \\
CaO + H₂O + 2NH₄Cl & \rightarrow CaCl₂ + 2NH₂OH \\
MgO + H₂O + 2NH₄Cl & \rightarrow MgCl₂ + 2NH₂OH \\
NH₄OH + NaCl & \rightarrow NH₄Cl + NaOH
\end{align*}
\]

The calcined and washed products were dried at 100°C, purified by bromoform, weighed and analysed.

A number of chemical and instrumental methods of analysis were used for the quantitative determination of major and minor element components of the present phosphate ore, using a strongly cationic ion exchange resin column in the hydrogen form (12). Phosphate ions were determined by the citromolybdate method (13) while sulphate ions by the barium chloride method (14). Calcium, magaesium, iron and aluminium were determined by EDTA titration (15). For the analysis of silica, ferrous iron fluorine, carbon dioxide, organic matter, OH⁻ and OH⁺, special treatment of a powdered sample was every time used. The procedure used for their determination was described in detail by Shapiro and Brannock (16), sodium and potassium were determined by flame photometrically (17) while titanium was estimated spectrophotometrically (18). Finally chloride ions were analyzed by measuring the turbidity produced by colloidal AgCl (19).

From both the obtained chemical analysis results and petrographic examination of representative thin sections the model or normative minerals of the studied ores can be calculated using mostly the assumption adopted by Anwar et al (20).
The distribution and abundance of trace elements in the samples were studied by radioactivation analysis. An international United State Geological Survey (USGS) standard sample (W. 1) was irradiated with each sample. The complete chemical analysis of which is published (21).

A known weight of each sample (∼ 0.2 g) was packed in a thin aluminium sheet, together with the standard. Samples were irradiated in the vertical dry channel of ET. RR-1 reactor of the Nuclear Research Centre at Inshas. Irradiation time was about 35 hours at a neutron flux of about 10^{22} n. cm^{-2}. sec^{-1}. The delay time was about 48 hours. Gamma spectra from samples and standard were measured using a 30 cm^2 Ge (Li) detector together with a 4096 PDP-11/05 computer based multichannel analyzer (Digital) and the necessary electronics (Nuclear Enterprises–Ortec and Canberra). A standard curve in the range of the measured isotopes was done before and after each measurement.

The identities of the detected elements producing γ-rays when activated were established by measurements of γ-ray energy and of half life, whereas the concentrations of the elements were calculated for all principal γ-lines by reference to the standard according to the following equation:

\[ W_2 = \frac{W_1 A_2 M_1}{A_1 M_2} \]

where \( W_1 \) is the known concentration of a certain isotope in the standard.

\( W_2 \) is the unknown concentration of the same isotope to be determined.

\( A_1 \) is the calculated area under the known peak after subtracting the background in the standard.

\( A_2 \) is the calculated area under the known peak after subtracting the background in the standard.

\( M_1 \) is the weight in gms of the standard sample.

\( M_2 \) is the weight in gms of the sample under investigation.

Since the half life of the isotopes under investigation is very much longer compared to the measuring periods and a standard is used there is no correction for decay of the activities \( A_1 \) and \( A_2 \).
In case of elements which are absent or not quantitatively given in the international standard, spectroscopy pure elements were added as internal standard. For elements which are absent in the international standard and the addition of their spectroscopy pure grade was impossible, equation (5) was used.

It is clear from equation (5) that a correction factor referred to as K factor is used. This factor is mainly due to the change in the absolute value of the neutron flux at the position of irradiation. An isotope of known concentration in the international standard is used. The verification of the used equation is as follows.

$$\text{Activity} \equiv \frac{W}{M} \times N \times a \times \varnothing \times \sigma \times 10^{-24} \times B \times (1 - e^{-0.693t_{fr}}) \times e^{-0.693t_{d} \over T_{1/2}} \tag{1}$$

$$\text{Activity} \propto \frac{A}{\gamma}$$

$$\text{Activity} = k_1 \times \frac{A}{\varepsilon} \tag{2}$$

Substitution of the value of activity from equation (2) in equation (1) we get

$$\frac{k_1A}{\varepsilon} = \frac{W}{M} \times N \times a \times \varnothing \times \sigma \times 10^{-24} \times B \times (1 - e^{-0.693t_{fr}}) \times e^{-0.693t_{d} \over T_{1/2}} \tag{3}$$

from equation (3) we can get the \( k_1 \) factor for the known isotope in the standard.

$$k_2 = k_1 \times \frac{\text{measured area of the peak after subtracting the background}}{\text{measured area of the peak after subtracting the background}} \tag{4}$$

from equation (4) we can obtain the \( k_2 \) factor of the isotope in the sample, and equation (3) becomes,
\[
\frac{k_2A_2}{\varepsilon} = \frac{W_2}{M} \times N \times a \times \varnothing \times \sigma_c \times B \times \left( 1 - e^{-\frac{0.693t_{Ir}}{T_{1/2}}} \right) e^{-\frac{0.693t_d}{T_{1/2}}} \tag{5}
\]

where \( A_2 \) is the area of the peak after subtracting the background,

\( W_2 \) = is the unknown concentration,

\( M \) = Molecular weight

\( N \) = Avogadro number \((6.023 \times 10^{22})\)

\( a \) = percent abundance

\( \sigma_c \) = the neutron capture reaction cross sections in barns \((10^{-22} \text{ cm}^2)\)

\( \varnothing \) = thermal neutron flux \(22 \text{ neutron cm}^{-2} \text{ sec}^{-1}\).

\( t_{Ir} \) = irradiation time in min,

\( t_d \) = Decay time in min,

\( T_{1/2} \) = Half life in mins\(^{23}\),

\( B \) = Branching ratio\(^{23}\),

\( \varepsilon \) = Relative efficiency of the Ge (Li) detector taken from the efficiency curve\(^{22}\).

\( k_2 \) = Correction factor taken from equation (4).

**RESULTS AND DISCUSSION**

Complete chemical analysis of the final calcined phosphate concentrate together with the original ore sample as well as their calculated potential mode of minerals are reported in Table (1). Nuclear data for the elements determined together with their concentrations are given in Table (2). Gamma spectra obtained from a standard W. I. and the studied phosphate samples are shown in Figs. (1–3).

As shown from Table (1) the ore sample contains 8.19 % dolomite and 4.30 % calcite and hence calcination should be used in the present study. Moreover, the calcined ore contains 9.20 % silicate and silica, accordingly the purification of the phosphate mineral by bromoform is essential before its analysis. The phosphate mineral (Collophane) increased from 66.40 to 84.13 % upon calcination, i.e. an increased factor of 1.27.
### Table 1. Chemical Assay and Potential Mode of Minerals for Wassif Original and Calcined Ore.

<table>
<thead>
<tr>
<th>Element</th>
<th>Safaga ore (Wassif)</th>
<th>Potential Mode of Minerals %</th>
<th>Safaga ore (Wassif)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Calced</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>12.03</td>
<td>8.48</td>
<td>T.C.P. (Ca₃PO₄)₂</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>27.36</td>
<td>34.87</td>
<td>CaF₂</td>
</tr>
<tr>
<td>CaO</td>
<td>43.14</td>
<td>45.96</td>
<td>Collophane</td>
</tr>
<tr>
<td>MgO</td>
<td>1.78</td>
<td>—</td>
<td>Ca₃(PO₄)₂.CaF₂</td>
</tr>
<tr>
<td>FeO</td>
<td>0.42</td>
<td>—</td>
<td>Ca₅O₄·2H₂O</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.18</td>
<td>0.86</td>
<td>Gypsum</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.79</td>
<td>1.19</td>
<td>CaCl₂</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.22</td>
<td>0.15</td>
<td>Dolomite</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.92</td>
<td>—</td>
<td>CaMg (CO₃)₂</td>
</tr>
<tr>
<td>SO₂</td>
<td>1.55</td>
<td>0.97</td>
<td>Calcite, CaCO₃</td>
</tr>
<tr>
<td>F⁻</td>
<td>3.25</td>
<td>3.25</td>
<td>Organic Matter</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.26</td>
<td>0.34</td>
<td>—</td>
</tr>
<tr>
<td>CO₂</td>
<td>6.55</td>
<td>0.79</td>
<td>Fe₂O₃·3H₂O</td>
</tr>
<tr>
<td>OH⁻</td>
<td>0.58</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Organic Matter</td>
<td>0.47</td>
<td>—</td>
<td>Silicate + SiO₂</td>
</tr>
<tr>
<td>OH⁺</td>
<td>7.50</td>
<td>0.80</td>
<td>—</td>
</tr>
</tbody>
</table>

Total 99.88 | 98.96 | Total 99.20 | 99.62

+ (—) not detected.

### Table 2. Nuclear Data and Concentration Results of Trace Elements In the Studied Phosphate Samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>Product</th>
<th>Half-life</th>
<th>Photo peaks used in Kev.</th>
<th>Conc. p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wassif</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>original</td>
</tr>
<tr>
<td>Cerium</td>
<td>¹⁴⁷Ce</td>
<td>33.0h</td>
<td>144.9</td>
<td>4.76</td>
</tr>
<tr>
<td>Barium</td>
<td>¹³¹Ba</td>
<td>11.6d</td>
<td>56.55, 373.1,396.3</td>
<td>948.94</td>
</tr>
<tr>
<td></td>
<td>¹³³Ba</td>
<td>1.62b</td>
<td>275.9,496.3</td>
<td></td>
</tr>
<tr>
<td>Lutetium</td>
<td>¹⁷⁷Lu</td>
<td>143d</td>
<td>176.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>¹⁷⁷⁷Lu</td>
<td>155b</td>
<td>113,128.6,204.3</td>
<td>1</td>
</tr>
<tr>
<td>Uranium</td>
<td>²³⁹Np</td>
<td>2.35d</td>
<td>228.1</td>
<td>64</td>
</tr>
<tr>
<td>Chromium</td>
<td>⁵¹Cr</td>
<td>27.8d</td>
<td>320.1</td>
<td>114.79</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>¹⁴⁰La</td>
<td>1.672d</td>
<td>328.8,482.2</td>
<td>127.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>815.8</td>
<td></td>
</tr>
<tr>
<td>Hafnium</td>
<td>¹⁷⁷Hf</td>
<td>70d</td>
<td>343.6</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>¹⁸⁷Hf</td>
<td>42.5d</td>
<td>133.0,482.2</td>
<td>156.22</td>
</tr>
<tr>
<td>Zirconium</td>
<td>⁹⁰Zr</td>
<td>65.5d</td>
<td>724.2,756.9</td>
<td>4.81</td>
</tr>
<tr>
<td>Europium</td>
<td>¹⁵⁵Eu</td>
<td>7.9y</td>
<td>1374.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>¹⁵⁸Eu</td>
<td>14.1y</td>
<td>1407.9</td>
<td></td>
</tr>
<tr>
<td>Scandium</td>
<td>⁶⁵Sc</td>
<td>84d</td>
<td>889.3,1120.5</td>
<td>7.15</td>
</tr>
<tr>
<td>Tin</td>
<td>¹⁷⁷Sn</td>
<td>9.62d</td>
<td>1087.4</td>
<td>1.91</td>
</tr>
<tr>
<td>Cobalt</td>
<td>⁶⁵Co</td>
<td>5.26y</td>
<td>1173.2,1332.5</td>
<td>3.33</td>
</tr>
</tbody>
</table>

+ (—) not detected
It is clearly seen from Table (2) that the trace elements Ce, U, Hf, Lu, La, Zr, Sc, Cr and Co increased with the same factor of the phosphate mineral concentration (1.27). This might suggest that these elements probably owe their abundance to the phosphate mineral itself.

Barium is actually one of the elements reported to be associated with the phosphate mineral itself. It undoubtedly substitute for Ca in the mineral. However, its decrease in the calcined phosphate product indicates that it has been partially replacing Ca in the calcite and dolomite structure of the gangue ore.

Europium like other rare earth elements should substitute Ca in the apatite lattice (1). However, its complete absence in the calcined product suggests that Eu might be associated with the eliminated minerals as calcite, dolomite and the organic matter.

CONCLUSION

Calcination, quenching and ammonium chloride washing operations proved to be successful beneficitation method for calcareous phosphate ores.

On the other hand, it is plausible that neutron activation analysis is a powerful non-destructive technique for the determination of elements particularly the rare earths. As shown from the results 0.59 part per million of Hafnium could be analyzed in the original sample.

The determination of the concentration of trace elements on the original and calcined sample made possible the assignment of their occurrence, i.e whether in the phosphate mineral or the gangue minerals

ACKNOWLEDGMENT

The authors wish to thank Prof. Dr. A.A. El-Kady and the staff of the Nuclear Physics Department Atomic Energy Authority, Egypt, for the facilities they offer during this work.
Fig. 1. Gamma Ray Spectrum of Standard Sample (W)
Fig. 1 (2) Gamma Ray Spectrum of Wessi Phosphate

Channel Number

Counts / Channel $\times 10^3$

- 320.1 Kev Cr$^{51}$
- 343.6 Kev Hf$^{175}$
- 373.1 Kev Bd$^{131}$
- 396.3 Kev Bd$^{133}$
- 482.2 Kev Hf$^{181}$
- 724.2 Kev Zr$^{95}$
Fig. (2) Gamma Ray Spectrum of Wassef Phosphate Ore

COUNTS / CHANNEL x 10^3

Channels:
- 756.9 Kev Zr^95
- 815.8 Kev La^{140}
- 8893 Kev Sc^{46}
- 1099.3 Kev Fe^{59}
- 1120.5 Kev Sc^{46}
- 1173.2 Kev Co^{60}
- 1274.8 Kev Eu^{154}
- 1291.6 Kev Fe^{59}
- 1333.2 Kev Co^{60}
- 1407.9 Kev Eu^{152}
- 1596.6 Kev La^{140}

CHANNEL NUMBER
Fig. 3: Gamma Ray Spectrum of Calcined Wassef Phosphate Ore.

Key points:
- 724.2 Kev Zr 95
- 756.3 Kev Zr 95
- 889.3 Kev Sc 46
- 1099.3 Kev Fe 59
- 1120.5 Kev Sc 46
- 1173.2 Kev Co 60
- 1291.6 Kev Fe 59
- 1332.5 Kev Co 60

Counts / Channel $\times 10^3$
References